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U. S. DEPARTMENT OF AGRICULTURE,

BUREAU OF SOILS—BULLETIN No. 51.
MILTON WHITNEY, Chief

ABSORPTION OF VAPORS AND GASES BY SOILS.

BY

HARRISON E. PATTEN AND FRANCIS E. GALLAGHER.



WASHINGTON:
GOVERNMENT PRINTING OFFICE.
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BUREAU OF SOILS.

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LETTER OF TRANSMITTAL

U. S. Department of Agriculture,
Bureau of Soils,
Washington, D. C., January 14, 1908.

SIR: I have the honor to transmit the manuscript of a technical article entitled "Absorption of Vapors and Gases by Soils," by Messrs. Harrison E. Patten and Francis E. Gallagher. It contains a historical review of the subject, together with experimental studies on the conditions which determine the quantity and rate of gaseous absorption by soils.

The article gives much valuable information which should be made available to the public. In accordance with your suggestion it has been gone over carefully with Assistant Secretary Hays, who authorizes me to state that he concurs in my recommendation for its

publication.

Respectfully,

MILTON WHITNEY, Chief of Bureau.

Hon. James Wilson, Secretary of Agriculture.



PREFACE.

In the continuation of the studies on absorption which have been carried on in this Bureau, it has been deemed desirable to direct attention especially to the absorption of gases by soils, and the present bulletin contains a description of certain special studies on this subject by Messrs. Patten and Gallagher.

That soils have a high absorptive power for gases, and show a direct selective absorption from gas mixtures as well as from liquid solutions, has long been known, and this fact has generally been recognized as having an important agricultural and geological significance. But up to the present it can not be said that agricultural investigators have given the question the consideration which its practical importance warrants.

In the present bulletin the absorption of the principal gases by various types of soils and the rate at which such absorption takes place have been brought out in such a manner that practical workers in soil problems will be able to use the results to advantage. Special significance must be attached to the absorption of water vapor, and in this bulletin the principal facts now known from the investigations of former workers or of the authors of the bulletin themselves are brought together in such shape that they are available not only for practical workers, but for the further investigation of scientific workers.

The relation between the absorption of water vapor on the one hand and the evaporation of water from that soil has been carefully investigated, and the laws controlling it have been clearly brought out; and the influence of soluble materials contained in the soil as affecting these laws has been shown. The significance of cultural methods as affecting either the absorption of water vapor or its evaporation has been shown. And finally, the important practical fact has been established that the wilting point—or that water content of the soil at which plants can no longer thrive and which has been shown elsewhere to be a physical factor of the soil—marks a water content higher than that which the soil can attain by direct absorption from a humid atmosphere, even though this latter be maintained at the point of saturation.

The laws governing the absorption of other gases or vapors appear in general to be very similar to those governing the absorption of water vapor, and it may now be safely claimed that the broad subject of absorption of vapors by soils has been brought to a satisfactory state as regards not only our theoretical knowledge of the principles involved and their importance to practical agriculture, but also as they bear upon the practical methods of control.

FRANK K. CAMERON.

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ABSORPTION OF VAPORS AND GASES BY SOILS.

PREVIOUS WORK.

INTRODUCTION.

It is well known that charcoal absorbs enormous volumes of gases from putrefying animal matter, and the similar power of soils to take up odors from excreta has been utilized from the earliest times.

The term absorption includes adsorption upon the surface, possible penetration of vapor into the solid, and retention of liquid in the angles formed between adjoining particles. A short review of the development of our knowledge of gaseous absorption is helpful here in bringing to mind the experimental facts and the varying explanations offered in connection therewith.

ABSORPTION OF GASES.

Fontana in 1777 established the fact that numerous porous bodies retain gases upon their internal surface, but did not deduce regularities from his data.

Morozzo, Rouppe, and Norden^a confirmed his observations in 1800, but de Saussure, ^b during 1812 to 1814, was the first to investigate this field extensively. He heated his absorbent material to redness before using, to expel residual gases, and then subjected the weighed absorbent to the action of a gas, under known temperature and pressure conditions. He drew the following conclusions: (1) The porous bodies investigated absorb gases; (2) the degree of absorption varies with the form and magnitude of the pores; (3) different substances possess a different absorption capacity; (4) the same substance absorbs different quantities of different gases; (5) easily condensed gases are in general absorbed more easily; (6) absorption decreases as temperature increases; (7) at higher pressure more gas is absorbed than at lower pressure; (8) heat is evolved during the process of absorption.

To these fundamental observations Smith adds: (1) Charcoal exercises a selective absorption toward mixtures of gases; for a con-

a O. Lehmann, Molekular-physik, II part, 83.

^b Ann. Phys. Gilbert, **47**, 113 (1814).

c Ann. Chem., Suppl. 2, 262 (1862-1863).

siderable time oxygen alone is absorbed from air; (2) charcoal saturated with nitrogen and then placed in other gases first gives up a part of the nitrogen before absorbing the second gas; (3) charcoal saturated with oxygen does not give up the gas, either upon warming or treatment with boiling water, but under these conditions carbon dioxide is evolved rather than oxygen.

Stenhouse, a too, has studied the absorption of gases by charcoal made from various materials; his figures, given in Table I, represent the number of cubic centimeters of gas absorbed by 1 gram of charcoal. Wood charcoal shows a higher absorption for the gases used than does peat or animal charcoal, with the exception of hydrochloric acid gas, which is taken up in greater volume by peat.

Table I.—Absorption of gases by charcoal, according to Stenhouse.

Con	Kine	d of cha	rcoal.
Gas.	Wood.	Peat.	Animal.
Ammonia. Hydrochloric acid. Sulphurous. Carbonic acid. Oxygen.	C. c. 98. 5 45. 0 32. 5 14. 0 0. 8	C. c. 96. 0 60. 0 27. 5 10. 0 0. 6	C. ic. 43. 5 17. 5 5. 0 0. 5

Dewar^b has found that charcoal and lampblack are nearly equal in absorbing power for gases at the temperature of liquid air, and that graphite is only one-fourth as good an absorbent.

ABSORPTION OF AIR.

Reichardt and Blumtritt^c showed that nitrogen is absorbed to a much greater extent by soils and soil constitutents than is oxygen and that each gas is retained to a different degree by different substances—a clear indication of the selective power which solids and gases mutually exert in absorption reactions.

ABSORPTION OF WATER VAPOR BY SOILS.

When a soil is saturated with water by rain, part of the water percolates away to lower levels, and another part of the water evaporates from the surface.

With a view to correlating the capacity of soils to resist drying out, with their composition and with their productiveness, Schübler^d determined the water vapor absorbed by various soils and soil constitutents from a nearly saturated atmosphere during 24 hours. This absorption process is evidently the reverse of drying out, but gives a

a Cited by Johnson, How Crops Feed, p. 160.

b Chem. News, 94, 174 (1906); Proc. Roy. Soc., 74, 130 (1904).

^c Jour. prakt. Chem., 98, 476 (1866).

d Cited by Johnson, How Crops Feed, pp. 161-162, 1870.

measure of the speed with which a dry soil takes up the first portions of water vapor, and this speed is clearly an indication of the strength with which the water is held by each soil. Thus, he found that 1,000 parts of soil absorbed parts of water as follows: Quartz sand, coarse, 0; gypsum, 1; calcareous sand, 3; plow land, 23; clay soil (60 per cent clay), 28; slaty marl, 33; loam, 35; fine carbonate of lime, 35; heavy clay soil (80 per cent clay), 41; garden mold (7 per cent humus), 52; pure clay, 49; carbonate of magnesia (fine powder), 82; humus, 120.

Similarly Davy^a gives the quantity of moisture taken up during one hour exposure to the air by soils which had been dried at 212° F. as follows, in parts of water per 1,000 parts of soil: Sterile soil of Bagshot heath, 3; coarse sand, 8; fine sand, 11; soil from Mercy, Essex, 13; very fertile alluvium, Somersetshire, 16; extremely fertile soil of Ormiston, East Lothian, 18.

From these results it may be concluded that the absorptive capacity of soil for water vapor is generally higher the finer the texture of the soil and the greater its content of humus. It appears, too, that productive soils have a very considerable capacity for water vapor, while the poor soils range much lower.

Regarding the effect of temperature upon the quantity of water vapor absorbed, Knop^a has shown that at higher temperature the absorption is very considerably decreased. A sandy soil from Moeckern, Saxony, absorbed in parts of water per 1,000 parts of soil the following quantities of moisture: At 55° F., 13; at 66°, 11.9; at 77°, 10.2; at 88°, 8.7.

The experiments of Ammon^b likewise show that the absorption of water vapor by soil constituents decreases as the temperature rises. The relative absorption at any one temperature of the substances used decreases in the order, ferric hydroxide, humus, kaolin,

calcium carbonate, gypsum.

Von Dobeneck has studied in great detail the conditions which determine the absorption of water vapor and gases in general by various soil constituents and admixtures of the same, with the following results: (1) The absorption is greater the finer the particles of the solid; but this increase is not directly proportional to the increase in surface, since large grains absorb relatively more gas than would be expected from the surface exposed. It should be remembered, however, that great error is introduced when the surface of a powder is calculated from the average diameter of its granules. (2) He found that adsorption and hygroscopic retention of moisture upon surfaces, which were then looked upon as different, are subject to the

a Cited by Johnson, How Crops Feed, pp. 161–162, 1870.

b Forsch. Agr.-Phys., 2, 36 (1879).

c Forsch. Agr.-Phys., 15, 163 (1892).

same controlling conditions. (3) The different soil constituents all possess a considerable absorption capacity, but gases are absorbed to a different degree by each solid substance. (4) Mixtures of these soil constituents absorb gases additively; that is, each soil material exerts its absorptive effect independently of the rest of the soil about it. (5) Absorption decreases with rise in temperature and is very nearly proportional to the reciprocal of the partial pressure. (6) For atmospheres of the same relative humidity, the temperature has little effect upon the mass of water absorbed; the absorption increases with increasing relative humidity, and at 20° C. the rise in absorption for equal per cent increments in the relative humidity is greater the nearer the interval lies to the point of saturation (100 per cent humidity). (7) Soil constituents moistened with water absorb gases in greater quantity than the same mass of water alone.

Van Bemmelen a has determined the absorption of water vapor by soils and inorganic oxides, especially such as yield gelatinous hydrates with water, with reference to (1) the influence of original water contained in the soil or solid oxide upon the quantity of water it can vet absorb; (2) the effect of vapor pressure upon absorption and liberation of moisture; (3) the structure and history of the oxide as related to its absorptive power. He used the oxides, SiO₂, SnO₂, MnO₂, Al₂O₃, Fe₂O₃, Cr₂O₃, BeO, MgO, and CuO and various soils. His results in general indicate that the absorption of water vapor increases with the vapor pressure, but is not simply proportional to it; that the fineness of the grains of a partially hydrated oxide has little influence upon its absorption—an effect to be expected where imbibition takes place; that the moist oxides expand as more water is absorbed and contract as this water evaporates from them in an atmosphere of lower vapor pressure; that some oxides form a translucent jelly when they contain a certain quantity of water, and this translucence indicates that the jelly is made up of fine cells. He concludes that the existence of definite chemical hydrates in these noncrystalline jellies is as yet undemonstrated and extremely improbable.

Van Bemmelen's reason for so thoroughly investigating these gelatinous inorganic hydrates is that much of the absorptive power of a soil is due to their presence, occasioned by the disintegration of minerals subject to weathering. His results on the absorption of water vapor by soils are similar to those obtained with these inorganic oxides, and agree in general with the results of earlier investi-

^a Zeit. anorg. Chem., 5, 467 (1893); Ber. deutsch. chem. Ges., 13, 1467 (1880); Jour. prakt. Chem., 23, 324, 379 (1881); 26, 227 (1882); Rec. Trav. Chim. Pays.-Bas, 7, 1 (1888); Jour. prakt. Chem., 46, 497 (1892); Zeit. anorg. Chem., 18, 122 (1898); 20, 185 (1899); 23, 111–321 (1900); Sitzungsber. d. K. Akad. d. Wiss., Amsterdam, Nov. 26, 1902; Arch. Néel. (2), 10, 267 (1906). See also Cross, On the Reformation of Hydrates, Jahresb., 1879, 179; also, Spring and Lucion, Zeit. anorg. Chem., 2, 195 (1892).

gators. Each soil shows its own peculiar power of absorbing water vapor—the finer the soil grains the greater the absorption; the presence of individual soil constituents of high absorptive power, of course, raises the absorption in proportion to the amount of each in the soil.

According to Hilgard,^a the hygroscopic moisture of a soil may vary from 2.48 per cent to 21 per cent, depending upon its composition. He has criticized the experiments of Schübler, Knop, and others, who found that absorption of water vapor decreases with rise in temperature. Hilgard finds that exactly the reverse is the case; soils exposed to an atmosphere saturated with water vapor absorb more moisture at high temperature than at low.

An attempt to discriminate between moisture held by a powder as "hygroscopic moisture" and water in the capillary spaces meets with difficulty.^b We have no sharp experimental method of ascertaining what fraction of the water is retained on the surfaces of the grains. This is especially so as an even distribution of moisture throughout the powder is hard to secure, and failing of this the powder is balled together and holds part of the liquid in its capillary spaces between the grains.

Briggs^c determined the quantity of water vapor absorbed by quartz grains of various degrees of fineness, and from the mechanical analysis of each powder calculated the surface presented, and thus found the thickness of the layer of adsorbed water. Assuming the density of the film as uniform and equal to unity and postulating an even distribution of the water over the entire surface, the maximum thickness obtained was 2.66×10^{-6} cm. in an atmosphere within 1 per cent of saturation at 30° C. He concludes that the adsorption is not due to soluble bodies present upon the surface of the quartz, as Warburg and Ihmori have suggested, but to the mutual attraction of quartz and water.

Parks ^d calculates the thickness of the water film upon glass wool as 13.3×10^{-6} at 15° C. Trouton ^e and O. Masson and E. S. Richards ^f have carefully determined the conditions under which cotton absorbs moisture. Trouton suggests that the water vapor is condensed to liquid upon the surface of the cotton. Masson and Richards find that cotton containing a definite proportion of moisture resembles

a"Soils," pp. 196, 198 (1906).

b Soyaka, Forsch. Agr.-Phys., 8, 1 (1885); Whitney, Agricultural Science, 3, 199 (1889); Katao, Ueber die Wasserbewegung in Boden, Bul. Col. Agr., Imp. Univ. Tokyo, Vol. 3, No. 1 (1897); Briggs, Bul. No. 10, U. S. Dept. of Agr., Division of Soils (1897).

c Jour. Phys. Chem., 9, 617 (1905).

d Phil. Mag. (6) 5, 519 (1903); also (6) 4, 240 (1902).

e Proc. Roy. Soc. London, 77, Ser. A, 292 (1906).

f Ibid., 78, Ser. A, 412-429 (1906).

an aqueous solution in that it exercises a vapor pressure which is at different temperatures a constant fraction of that of pure water.

In this connection it is interesting to note that Bunsen ^a found that glass fiber continued to give up moisture on heating until a temperature of 503° C. was reached; similarly, Day and Allen ^b state that a temperature of 600° to 800° C. (a low red heat) is required to remove hygroscopic moisture from minerals. From the fact that moisture is retained upon the surface of these substances at high temperature it may be inferred that the attraction between the substance and water is greater than the vapor pressure, which at such temperatures amounts to hundreds of atmospheres.

ABSORPTION OF WATER VAPOR.

STATEMENT OF THE PROBLEM.

The general problem before us is to find the relation of climatic humidity to soils. In nature a system is rarely in a state of equilibrium, and more or less rapid changes in the distribution of the constituents are in progress. Still, in the present instance, definite laboratory conditions for the equilibrium between soil moisture and water vapor in the air above it will afford a very fair approximation to field conditions, and by taking measurements upon the rate of approach to equilibrium we also secure an insight into the nature and rate of change in soil moisture during evaporation or absorption when sudden climatic changes disturb the approximate equilibrium between atmospheric moisture and soil moisture. Such displacement of equilibrium may be due to currents of air bringing a more or less humid atmosphere from a distance, or to heat changes accompanied by precipitation on cooling, or greater saturation capacity of the air for water on heating.

The first variation—change in humidity—may be experimentally reproduced by placing several equal portions of a soil of known moisture content in desiccators whose individual atmospheric humidity is maintained practically constant by sulphuric acid, differing in strength for each desiccator and thus giving a range of humidity from the very low partial pressure of concentrated acid to the vapor pressure of water at the temperature chosen for the experiments.

The second source of variation—heat changes—may be studied by running equilibrium experiments similar to those just described, but at different temperatures, and comparing the quantities of moisture in soil and in vapor above it at each of these temperatures.

a Ann. Phys., 24, 321 (1885).

b Pub. Carnegie Inst. of Washington, No. 31, pp. 56-57; Am. Jour. Sci. (4), 19,93 (1905).

EVAPORATION STUDIES.

Experimental methods.

The evaporation of water from soils was determined under different degrees of humidity, secured by maintaining the soils in small weighing bottles in desiccators containing sulphuric acid in varying concentration. Quantitative preliminary work showed the need of accurate temperature control; consequently the experiments here described were carried out in a double-walled air thermostat heated by incandescent electric lights, the current being controlled by a Geer thermoregulator ^a and the air circulated by an electric fan. (The temperature was recorded, when desired, by a thermograph. The temperature could thus be held constant and within 0.1° C. for days.)

Diffusion constant for the desiccators.

As regards the diffusion of water vapor from the soil in the weighing bottle through the atmosphere of the desiccator down to the surface of the sulphuric acid, it may be stated that in general this takes place at a very constant rate. This constancy will be evident from an inspection of the curves given in figures 1, 2, and 3, for the evaporation of soils in atmospheres of different degrees of humidity. As may be expected, these curves are linear during the time when evaporation is taking place from the larger soil tubes, but when the soil moisture begins to evaporate from the finer capillary spaces, the rate of evaporation, and consequently the diffusion constant itself, changes as evaporation proceeds. A variation in the value of this diffusion constant may also be due to a slight difference in the size of the mouths of the weighing bottles.

Experimental data.

The rate of approach to equilibrium of quartz flour, Podunk fine sandy loam, and Sea Island cotton soils over water and over sulphuric acid of different strengths at 25° C. is given in Tables II, III, and IV, respectively. The upper section of each table shows the loss of water from a wet soil as the evaporation proceeds, while the lower section gives the absorption by the same soil in dry condition under the same conditions of temperature and humidity. Thus if sufficient time be given, the same percentage of moisture will be found in the soil regardless of its previous moisture content; i. e., equilibrium is approached from both the wet side and the dry side. At the head of each column in the tables is given the strength of sulphuric acid expressed in percentage by weight and the corresponding partial pressure of water vapor in millimeters of mercury.^b The evaporation data from the upper half of Tables II, III, and IV are plotted in figures 1, 2, and 3, for quartz, Podunk, and Sea Island soils, respectively, ordinates being percentage moisture in the soil reckoned upon its dry weight, and abscissas time in days.

^a Jour. Phys. Chem., 6, 85 (1902).

b Landolt and Börnstein, Tabellen.

Table II.—Change in moisture content of quartz flour exposed to atmospheres of different humidity at 25° C.

MOIST SOIL.

Strengt	h of sulphu	rie acid, v	vith equiva	lent part	ial pressur	e of wate	r vapor.	Water alone.		
	r cent 0 mm.			55.4 per cent = 6.0 mm. $42.55 per cent = 12 mm.$		29.84 per cent = 17.9 mm.		23.55 mm.		
Period.	Moisture content.	Period.	Moisture content.	Period.	Moisture content.	Period.	Moisture content.	Period.	Moistur	
Days. 0.00 .167 1.00 2.08 3.08 4.00 5.15 6.04 8.02 9.05 9.87 10.13 11.16 17.00 33.00	Per cent. 30.00 29.40 26.30 23.10 19.80 16.80 13.40 9.80 1.90 .50 10 .07		Per cent. 30.00 27.80 25.40 23.40 21.60 13.90 9.80 4.10 .09	Days. 0.00 1.04 2.10 3.08 4.04 8.00 13.00 17.00 19.20 23.00 25.00 26.00 27.00 30.00 33.00	Per cent. 30.00 28.50 27.20 25.80 24.60 20.00 13.80 9.50 6.90 2.80 1.20 .12 .11	Days. 0.00 1.04 2.11 3.09 4.04 8.00 13.00 21.20 23.00 33.00 38.00 46.00 52.00 97.00	Per cent. 30.00 29.20 28.50 27.80 27.20 24.80 22.00 11.70 11.00 8.20 4.30 1.30 1.30	Days. 0.00 1.01 2.11 3.04 6.04 13.00 27.00 97.00	Per cen 30. 0 29. 9 29. 8 29. 7 29. 5 29. 3 28. 6 28. 5 25. 4	

DRY SOIL.

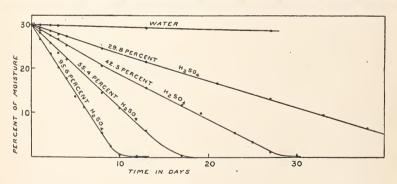


Fig. 1.—Curves for quartz flour, showing effect of humidity upon rate of evaporation.

Table III.—Change in moisture content of Podunk fine sandy loam soil exposed to atmospheres of different humidity at 25° C.

MOIST SOIL.

Strength	of sulphur	ic acid, v	vith equive	alent par	tial pressu	re of wat	er vapor.	Water alone.	
95.6 per cent =0.10 mm.		55.4 per cent =6.0 mm.		42.55 per cent =12 mm.		29.84 per cent =17.9 mm.		23.55 mm.	
Period.	Moisture eontent.	Period.	Moisture content.	Period.	Moisture eontent.	Period.	Moisture content.	Period.	Moistur
Days. 0.00 167 1.00 2.09 3.00 5.15 6.04 8.02 9.05 9.87 10.13 11.16 17.00 33.00	Per cent. 30.00 29.50 26.70 23.30 20.30 17.90 13.90 11.50 5.60 2.50 .70 .40 .30 .13		Per cent. 30.0 28.1 25.9 23.8 22.1 14.8 11.2 6.0 4 .3	Days. 0, 00 1, 04 2, 11 3, 09 4, 04 8, 00 13, 00 17, 00 19, 20 23, 00 25, 00 27, 00 30, 00 33, 00	Per cent. 30.00 28.70 27.50 26.80 25.20 20.60 15.70 11.90 9.80 5.70 3.50 1.10 .40 .43	Days. 0.00 1.04 2.11 3.11 4.04 8.00 13.00 21.20 23.00 33.00 38.00 46.00 52.00 97.00	Per cent. 30.00 29.20 28.50 27.80 27.20 24.60 16.80 13.30 9.70 6.50 2.50 .60 .51	Days. 0.00 1.01 2.12 3.12 6.04 13.00 27.00 55.00 97.00	Per cent 30.0 29.9 29.8 29.7 29.5 29.2 28.6 27.5 26.5

DRY SOIL.

0.0	0.30	0.0	0.3	0 0	0.3	0.0	0.30	1. 01 2. 12	0.30
13. 0 17. 0	. 16	10. 0 33. 0	.4	33. 0	. 4	3. 0 97. 0	.51	3. 12 6. 04	. 70
21. 0 33. 0	03							13. 00 27. 00	1.00
								55.00	1.10
			1	3				97. 00	1. 16 1. 24

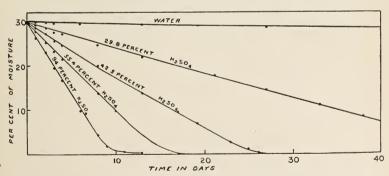


Fig. 2.—Curves for Podunk soil, showing effect of humidity upon rate of evaporation.

27876-Bul. 51-08-3

Table IV.—Change in moisture content of Sea Island cotton soil exposed to atmospheres of different humidity at 25° C.

MOIST SOIL.

Streng	th of sulphu	ricacid, v	vith equiva	ilent part	ialpressur	e of water	vapor.	Wate	r alone.
	94 per cent =0.10 mm.		55.4 per cent =6.0 mm.		42.55 per cent =12 mm.		29.84 per cent =17.9 mm.		5 mm.
Period.	Moisture content.	Period.	Moisture content.	Period.	Moisture content.	Period.	Moisture content.	Period.	Moisture content.
Days. 0.00 .167 .96 2.08 3.08 4.00 5.15 6.04 8.02 9.05 9.87 11.16 12.08 13.05 14.00 17.00 21.00 33.00	Per cent. 55. 00 54. 20 51. 60 48. 60 43. 20 40. 10 37. 50 30. 00 24. 00 17. 90 13. 70 9. 20 6. 40 2. 10 98 34	Days. 0.00 1.01 2.10 3.08 4.00 10.10 13.00 17.00 19.20 23.00 25.00 27.00 30.00 33.00 52.00	Per cent. 55.0 52.9 50.5 48.4 46.5 37.4 33.1 27.6 17.6 11.2 4.6 3.5 3.1 2.9 2.9 2.8	Days. 0.00 1.04 2.09 3.08 4.04 8.00 17.00 19.20 23.00 27.00 30.00 33.00 33.00 46.00 52.00	Per cent. 55.0 53.2 51.4 49.8 48.3 42.1 35.0 29.4 26.1 20.4 15.0 10.5 6.6 4.7 4.4 4.2	Days. 0.00 1.03 2.11 3.09 4.04 8.00 13.00 21.20 27.00 33.00 46.00 97.00	Per cent. 55.00 54.10 53.30 52.10 51.90 49.30 46.30 41.20 37.70 34.10 25.50 6.08	Days. 0.00 1.10 2.11 3.14 6.04 8.00 10.10 13.00 55.00 97.00	Per cent. 55. 0 54. 8 54. 7 54. 6 54. 3 54. 0 53. 9 53. 7 49. 2 48. 5

DRY SOIL.

0. 0 1. 0 13. 0 17. 0 21. 0 33. 0	4. 40 4. 10 2. 90 1. 70 1. 00 . 47		4. 4 4. 6 4. 8 2. 9 2. 8				4. 4 4. 9 5. 4 5. 5 5. 9 6. 0 5. 6	0.00 1 01 2.13 3.12 4.04 6.00 8.00 10.10 13.00 27.00 55.00 97.00	4. 4 5. 1 5. 6 5. 9 6. 1 6. 6 6. 8 7. 2 7. 6 8. 6 9. 2 9. 7
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Discussion.

Evaporation from soils under different conditions of humidity in general proceeds regularly, as shown by the above curves, which are similar in form. The curves for Sea Island soil over 55.4 per cent sulphuric acid and over the concentrated acid (fig. 3) are displaced to the left in their lower portions. This effect is almost certainly due to the fact that the samples of quartz, Sea Island, and Podunk soils were run in the same desiccator. The latter two soils holding less water, reached the dry state first, and when they no longer gave up water to the surrounding atmosphere the rate of evaporation for Sea Island cotton soil increased, thus producing the displacement in

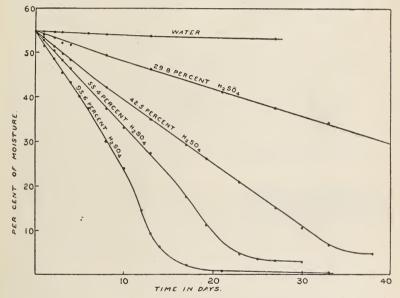


Fig. 3.—Curves for Sea Island cotton soil, showing effect of humidity upon rate of evaporation.

the curve. This observation emphasizes the necessity of closely regulating the conditions for evaporation studies.

The influence of the presence of organic matter in a soil is shown by a comparison of the evaporation curves for quartz, Podunk, and Sea Island soils over concentrated sulphuric acid. The presence of organic matter in Sea Island soil increases its water-holding power some 25 per cent above that of quartz or Podunk soil, but it does not decrease the rate of evaporation, for the Sea Island curves are very nearly parallel to those for Podunk fine sandy loam and for quartz.

The foregoing study is important in that it gives a valid basis for applying the experimental results determined for one humidity condition to any other humidity condition. Because of the high rate of evaporation and slow change in vapor pressure of the acid, it is preferable to use concentrated sulphuric acid in evaporation studies. Results thus obtained may be confidently used for general application.

The relation of the length of time required for a soil to dry out to the atmospheric humidity is of great agricultural interest. Equal changes in humidity correspond to very unequal periods required for a soil to dry. Thus, for quartz, 60 days would be required to reach an air-dry condition with an atmospheric humidity of 75 per cent: 26 days with 50 per cent humidity; 16 days with 25 per cent

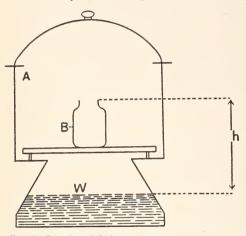


Fig. 4.—Drawing of desiceator containing soil sample.

humidity, and the proportionately long period of 10 days with 1 per cent humidity.

The rate of evaporation curves show, too, that wet soil in an atmosphere saturated with water vapor slowly loses weight. This loss may be due to several disturbing influences.

There is a slight difference in the vapor pressure of the water in the bottle B and the water W, caused by the weight of a column

of vapor of height h (see fig. 4). $P_b - P_w = hd$, where P_b and P_w are the vapor pressures at the level in the bottle and at the lower water surface W, respectively, and d is the density of the vapor. Although this value is very small, it is theoretically of interest and might enter into calculation when the time factor is large.

Small changes in temperature would cause loss of water from the weighing bottle containing moist soil. If the temperature rises a little this will first affect the desiccator near the outside wall, at A, figure 4. The increase in temperature momentarily reduces the relative humidity, thus disturbing the equilibrium. In order to restore equilibrium water vapor moves from the interior of the desiccator near B toward A. This produces at the same time evaporation of the water in B and of the water at W in the bottom of the desiccator. If a slight drop in the temperature within the thermostat now takes place cooling will first occur at A, followed by supersaturation and finally by condensation of moisture at A until equilibrium is again estab-

lished. This cooling, however, will not produce a condensation upon the surface of the soil equal in amount to the loss by evaporation due to rise in temperature. Thus a slow loss of water from soil will result.

The thermostat was heated by an incandescent electric lamp, consequently a black soil might absorb sufficient radiant energy to maintain its temperature slightly above that of the surrounding medium. The vapor pressure of the warmer soil moisture would be higher, and a distillation of water from B to W would result.

Opening the desiccator for estimation of the moisture in soil would reduce the humidity and cause evaporation from the soil when replaced after weighing.

ABSORPTION STUDIES.

Experimental data.

The absorption of moisture by air-dry soils in an atmosphere saturated with water vapor is shown by the data given in Tables II, III, and IV for quartz, Podunk fine sandy loam, and Sea Island cotton soils at 25° C. As stated above, these experiments were carried out with weighing bottles placed in a desiccator. A parallel set of experiments using shallow aluminum dishes showed that the dishes do not give so great gain in moisture as is obtained when weighing bottles are used. The three soils used here were in air-dry condition at the start; their moisture content in percentage is given in Tables II, III, and IV.

A set of absorption experiments was carried out, using other soils and soil separates which had been heated to constant weight at 110° C, and then placed in a saturated atmosphere at 28° C. This set was not subjected to such accurate temperature control as those given above, still the curves obtained by plotting gain in moisture against time of absorption are very regular and the data fairly characteristic. The data are given in Table V.

Table V.—Water vapor absorbed by soils from a saturated atmosphere at 28° C.

Period.	Galveston clay.	Hagers- town loam.	Marshall silt loam.	Norfolk sand.	Quartz.				
Days. 1 2 3 14 19 23 31 34 37 49	Per cent. 4.699 5.896 6.504 8.928 9.685 9.779 10.228 10.277 10.373 10.841	Per cent. 1.717 2.047 2.363 3.152 3.317 3.625 3.974 4.014 4.107 4.553	Per cent. 1, 823 2, 220 2, 455 2, 990 3, 160 3, 383 3, 603 3, 611 3, 713 4, 005	Per cent. 0, 169 220 240 322 334 354 390 416 440	Per cent. 0.144 .203 .245 .417 .420 .502 .574				
AREA PER GRAM.									
	Sq. cm. 3,280	Sq. cm. 2,270	Sq. cm. 2,320	Sq. cm. 300	Sq. cm. 1,260				

Discussion.

At the bottom of Table V is given the area of each soil in square centimeters per gram as calculated from its mechanical analysis.

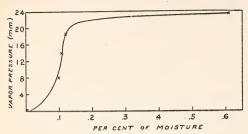


Fig. 5.—Curve showing variation of moisture in quartz flour with increase in atmospheric humidity.

This affords a rough comparison of soil texture with absorptive power, and shows that in a broad way the absorptive power is greater for soils of fine texture, as would be expected. Galveston clay absorbs three times the mass of water vapor that Marshall silt loam takes up, while

the calculated area of the clay per gram is not three times greater, but less than a third greater, than for the silt loam.

DEPENDENCE OF MOISTURE CONTENT UPON HUMIDITY.

Table VI contains a summary of the equilibrium points already

given in Tables II, III, and IV—that is, the percentage of moisture retained by each soil over each strength of sulphuric acid, a quantity which is practically the same as the percentage absorbed by the air-dry soil from air saturated with moisture over the different concentrations

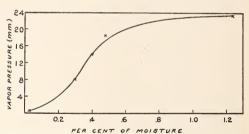


Fig. 6.—Curve showing variation of moisture in Podunk soil with increase in atmospheric humidity.

of sulphuric acid used. Of course, during the evaporation from the moist soil the sulphuric acid in each desiccator became diluted.

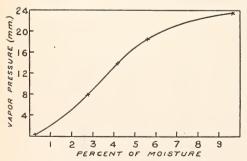


FIG. 7.—Curve showing variation of moisture in Sea Island cotton soil with increase in atmospheric humidity.

In Table VI is given the initial and final strength of each portion of acid and the corresponding partial pressures of water vapor over this acid. Opposite these acid percentages are found the moisture contents of each soil, quartz, Podunk, and Sea Island.

In figures 5, 6, and 7 curves are plotted from the

data given in Table VI, showing the variation in moisture content of each soil with increasing atmospheric humidity. Ordinates are in partial pressures of water vapor expressed in millimeters of mercury; abscissas percentage of water in the soil.

Table VI.—Variation of moisture content of soil with humidity under equilibrium conditions at 25° C.

Strength of s	ulphuric acid.	Qua	rtz.	Podu	ink.	Sea Island.	
Initial.	Final.	Drying out.	Absorbing moisture.	Drying out.	Absorbing moisture.	Drying out.	Absorbing moisture.
Per cent=Mm. 94.00 0.01 55.40 6.00 42.55 12.00 29.84 17.90 Water. 23.50	Per cent=Mm. 88.3 0.09 51.2 8.00 39.0 14.00 27.1 18.30 Water. 23.50	Per cent. 0. 07 . 09 . 11 . 12	Per cent, 0. 07 . 10 . 11 . 12 . 61	Per cent. 0. 04 . 30 . 43 . 51	Per cent. 0. 02 . 30 . 40 . 48 1. 24	Per cent, 0. 34 2. 80 4. 20 6. 08	Per cent. 0.47 2.80 4.10 5.60 9.70

The point on each of these curves figures 5, 6, and 7 corresponding to 23.5 mm., the partial pressure of water vapor at 25° C., may be high on account of the "dew point" effect produced by even slight temperature changes, as suggested in the previous discussion.

Because of the wide range through which the moisture content varies, the curve for Sea Island cotton soil in figure 7 is probably

the most correctly determined. Owing to its low percentage of abwater, errors sorbed caused by slight temperature changes greater relatively for quartz, and its curve in figure 5 is less accurate. These curves in figures 5, 6, and 7 resemble those given by van Bemmelen a for the absorption of water vapor by silicic acid at various partial pressures, save that for these soils no certain hysteresis effect is shown. However, we

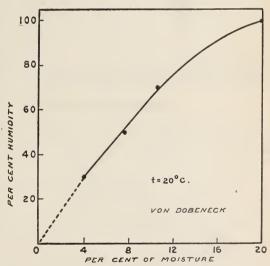


Fig. 8.—Curve showing variation of moisture in humus with increase in atmospheric humidity.

are here dealing with an adsorption effect rather than with imbibition, especially in the case of quartz flour; whereas van Bemmelen's hysteresis effect occurs with the colloidal silicic acid and is due mainly to imbibition; indeed, he gives data showing that the fineness of the silicic acid particles has no marked effect upon the mass of water vapor absorbed.

For comparison with this data, von Dobeneck's work upon the absorption of water vapor by humus in atmospheres of different humidity is given in Table VII. The equilibrium points are plotted in figure 8 and give a curve similar in form to that in figure 6 for the Podunk soil.

Table VII.—Change in moisture content of humus submitted to atmospheres of different degrees of humidity at 20° C., according to von Dobeneck.

Humidity 30 per cent.		Humidity 50 per cent.		Humidity 70 per cent.		Humidity 90 per cent.		Humidity 100 per cent.	
Period.	Moisture absorbed.	Period.	Moisture absorbed.	Period.	Moisture absorbed.	Period.	Moisture absorbed.	Period.	Moistur
Days.	Per cent.	Days.	Per cent.	Days.	Per cent.	Days.	Per cent.	Days.	Per cent
1	1.68	1	a 4, 91	1	a 8, 03	1	a 10, 85	1	a 16, 11
2	2.96	$\tilde{2}$	5, 77	2	8, 47	2	11. 28	2	16.49
3	3. 47	3	6, 41	3	8.74	3	11.65	3	16, 75
4	3. 62	4 5	6, 96	4	9.00	4 5	12.06	4	16.93
5	3. 68	5	7.36	5	9. 31	5	12. 48	5	17.09
6	3. 73	6	7. 60	6	9. 51	6	12.96	6	17.29
7	3.80	7	7.63	7	9.70	7	13. 44	7	17. 50
8	3.94	8	7.68	8	9. 77	8	13.94	8	17.71
9	3.99	9	7.74	9	9. 94	9	14.28	9	17.83
10	4. 01	10	7.75	10	10.16	10	14. 56	10	17.85
11	4. 03	11	7.76	11	10. 27	11	14.95	11	17.89
12	4.05			12	10.32	12	15. 24	12	17. 90
				13	10. 47	13	15. 27	13	17. 96
				14	10. 42	14	15. 36	14	18.02
				15	10.48	15	15. 44		
				16	10. 54	16	15. 49		
				17	10. 57	17	15. 55		
				18	10. 58	18	15. 59		
				19	10. 59	19	15. 63		
				20	10. 58	20	15. 67		

^aThe sample of humus after being saturated in an atmosphere of a given degree of humidity was placed in an atmosphere of higher humidity and allowed to reach equilibrium. This process was continued up to an atmosphere of 100 per cent humidity.

ABSORPTION OF OTHER VAPORS.

In Table VIII is given the percentage of toluene (C₆H₅.CH₃) vapor absorbed by Galveston, Hagerstown, Marshall, and Norfolk soils and quartz from a saturated atmosphere at 28° C. Similarly, Table IX contains the percentage of ether taken up by the soils at 27° C. from an atmosphere consisting entirely of ether vapor. Comparing these results with those given in Table V it is seen that Galveston clay has the same relative absorptive power for toluene and for water, although the mass of water vapor retained is almost exactly twice that of the The Hagerstown, Marshall, and Norfolk soils absorb toluene vapor to the extent of slightly less than half the mass of water vapor each soil can take up. Galveston clay absorbs about one-half more ether than water by weight, while the reverse is true of Norfolk sand, and the other two soils take up about the same quantity of ether as of Table X gives the absorption of water, ether, and toluene vapors at 28° C. by a soil separate fraction obtained in the mechanical analysis of soils a whose grains varied from 0.1 to 0.05 mm. in diame-

a See Bul. No. 24, Bureau of Soils, U. S. Dept. Agr. (1904).

ter. Here the absorption of ether vapor is slightly higher than that of water, and the toluene considerably lower. Still the quantities of all three vapors absorbed are of the same order of magnitude.

Table VIII.—Toluene vapor absorbed by soils from a saturated atmosphere at 28° C.

Period.	Galveston clay.	Hagers- town loam.	Marshall silt loam.	Norfolk sand.	Quartz.
Hours. 18.00 25.25 67.00 139.00 187.00 477.00	Per cent. 2, 400 2, 697 3, 797 4, 467 4, 791 5, 318	Per cent. 0.860 1.367 1.736 1.851 1.866	Per cent. 0.810 .853 1.297 1.529 1.615 1.759	Per cent. 0.078 .083 .117 .138 .167 .185	Per cent. 0. 112 . 192 . 272 . 285 . 285

Table IX.—Ether vapor absorbed by soils, at 27° C., 575 mm. pressure.

Period.	Galveston clay.	Hagers- town loam.	Marshall silt loam.	Norfolk sand
Days. 0.75 11.75 16.75 28.00 31.00	Per cent. 4. 320 4. 840 5. 015 5. 760 5. 870	Per cent. 2, 625 3, 580 3, 82 3, 995 4, 371	Per cent. 2, 320 3, 070 3, 310 3, 605 3, 895	Per cent. 0. 421 . 459 . 470 . 618 . 618

Table X.—Absorption of water, ether, and toluene vapors by a soil separate (0.1-0.05 mm.), at 28° C.

Period.	Toluene.	Ether.	Water.
Hours. 17. 75 25. 50	Per cent. C. 264	Per cent. 0. 481 . 515	Per cent. 0. 367 . 418
35. 00 42. 75 106. 75	. 343	. 699	. 539
114. 50 154. 25 162. 00 352. 00	. 405	. 763	. 609 . 624 . 718

ABSORPTION OF GASES.

Absorption of air.

Reichardt and Blumtritt a recovered the gas absorbed by various soils and soil constituents from the atmosphere and analyzed it to ascertain what proportion of each atmospheric gas was held fixed in the soil. Their results are given in Table XI, and show that nitrogen is absorbed to a much greater extent than oxygen, and that each gas is retained to a different degree by different substances; a clear indication of the selective power which solids and gases mutually exert in absorption.

Dewar ^b has shown that all the inert gases—argon, helium, neon, krypton—can be condensed in charcoal as effectively as ordinary gases at suitable pressure and temperature.

^a Jour. prakt. Chem., 98, 476 (1866).

b Proc. Roy. Soc., 74, 130 (1904).

Table XI.—Absorption of atmospheric gases by various substances, according to Reichardt and Blumtritt.

0.1	Gas per	Ratio, by volume.			
Substance.	100 grams.	Nitrogen.	Oxygen.	CO ₂ .	
Charcoal, air dry. Peat. Garden soil. Fe (OH)3, air dry. FesO3, ignited. Al (OH)3, air dry. Alumina, dried at 100° C. Clay. Clay, moistened. River silt. Magnesium carbonate.	39 69 11 33 29 40	Per cent. 100 44 65 26 83 41 83 65 60 68	Per cent. 0 5 2 4 13 0 17 21 6 0 7	Per cent. 5 3 3 7 6 5 6 1 3 3 3 3 2 2	

Absorption of oxygen.

In addition to the experiments of de Saussure, Smith, Stenhouse, and Reichardt and Blumtritt, several series of investigations have been carried out upon the absorption of oxygen gas. Joulin, a working with ignited charcoal, found that oxygen was so quickly absorbed. that measurements on the velocity of absorption were not possible with the means at his command. Baker b has shown that a temperature of 450° C, is required to recover the gas from charcoal which has absorbed dry oxygen, and that the gas thus obtained is mainly carbon monoxide, only a little carbon dioxide being formed. Dewar, on the other hand, by using a low-temperature bath of liquid air has succeeded in absorbing in charcoal more oxygen than nitrogen from the atmosphere, and upon warming the charcoal to ordinary room temperature again a large part of this oxygen is liberated, along with nitrogen, thus affording a ready means of obtaining oxygen from air by simply repeating the absorption and liberation process till the oxygen has the desired degree of purity. Richards and Rogers,^d too, have shown that zinc oxide derived from the nitrate, even when heated to very high temperatures, retains nitrogen and oxygen. Morse and Arbuckle confirmed these results, but found no evidence supporting Richards and Rogers's conclusion that the absorbed oxygen escapes more readily than the nitrogen. The zinc oxide was heated by Morse and Arbuckle to a temperature sufficient to melt cast steel and still retained per gram of oxide some 0.3 c. c. of gas whose composition varied—the nitrogen between 64.32 and 68.18 per cent, and the oxygen correspondingly, while the total volume of occluded gas was very nearly constant for eight different experiments.

a Compt. rend., 90, 741 (1880).

^b Jour. Chem. Soc., **51**, 249 (1887).

c Chem. News, 94, 174 (1906).

d Proc. Am. Acad., 28, 200 (1893).

^e Am. Chem. Jour., 20, 200 (1898).

Absorption of nitrogen.

The absorption of nitrogen by soils has been studied mostly in connection with the absorption of atmospheric gases. From the work of Reichardt and Blumtritt, cited above, it appears that in general nitrogen is absorbed by soils in greater quantity than oxygen. This fact is especially worthy of note, since the absorption of oxygen and nitrogen from air by water gives a higher ratio of oxygen to nitrogen in the solution than the 1:4 relation which exists in air. The explanation immediately suggested is that oxygen is converted to carbon dioxide in the soil by action of the decomposing organic matter. But the similar high absorptive power of aluminum hydroxide, ferric hydroxide, and magnesium carbonate for nitrogen indicates that this is a real phenomenon, since these substances have no way of masking their true absorptive power for oxygen by converting it chemically to carbon dioxide, as a soil does, or to other oxides. Gypsum, too, preserves the ratio 81:19 of nitrogen to oxygen when it absorbs these gases from the air.

Absorption of carbon dioxide.

The determination of the actual quantity of carbon dioxide taken up by a soil from air is difficult, since the absorbed oxygen acts upon the organic matter in the soil to yield carbon dioxide, and the decaying organic matter itself contains carbon and oxygen which adds still more carbon dioxide to the soil atmosphere. The absorption of carbon dioxide from an atmosphere containing this gas alone can be estimated by the reduction of vapor pressure, by a density determination of the gas, or by determining chemically its weight in a given volume of the gas before and after contact with the soil.

Reichardt and Blumtritt determined the per cent by volume of carbon dioxide absorbed by soils and soil constituents. They showed that it is probable that the oxygen of the absorbed air is converted to CO₂ in the peat; of 162 c. c. gas absorbed from air, 44 per cent appears as nitrogen, 5 per cent as oxygen and 51 per cent as carbon dioxide. A similar relation is seen for the garden soil, moistened clay, and river silt. The ignited ferric oxide and aluminum oxide both show higher absorption of oxygen than the hydrated oxides, and lower absorption of carbon dioxide. This indicates that the absorption of carbon dioxide is dependent to a considerable extent upon the presence of water in the absorbing material, further evidence being afforded by the higher absorption of carbon dioxide by the moist clay.

Scheermesser^a has stated that the amount of carbon dioxide absorbed by a dry soil is proportional to the amount of ferric oxide present, which would appear to be a generalization based on too few

observations. Von Dobeneck^a gives the carbon dioxide absorbed by soil constituents as follows:

Table XII.—Absorption of carbon dioxide by soil constituents according to von Dobeneck.

	CO ₂ absorbed at—			
Soil constituents, 100 grams.	0° C.	10° C.	20° C.	30° C.
Quartz. Kaolin. Humus. Fe (OH)3. CaCO3.	. 329 2. 501 6. 975	Grams. 0. 021 . 298 2. 125 5. 702 . 053	Grams. 0.023 .261 1.773 5.054 .034	Grams. 0. 022 . 215 1. 479 4. 274 . 019

Kayser^b attempted to express in absolute units the dependence of the absorption by glass fiber upon temperature and pressure. His aim was to measure the quantity of gas condensed by a known surface under definite temperature and pressure (and therefore with known concentration of the vapor phase) and to utilize this relation to estimate the surface of fine powders from the quantity of gas they absorb. But he was forced to abandon this, since adsorption is not dependent solely upon extent of surface, temperature, and pressure. He found (1) that glass fiber dried for a long time at high temperature adsorbs carbon dioxide, a few hours being required for saturation; (2) the adsorption increases with the pressure, and (3) decreases as the temperature increases.

A little later Bunsen, using similar materials (glass fiber and carbon dioxide), obtained results at variance with those of Kayser, as follows: (1) Glass is not saturated with carbon dioxide in days or months, but only after several years have elapsed. Thus 1 sq. cm. of glass adsorbed of carbon dioxide at the end of the first year, 3.15 c. c.; second year, 1.10 c. c. more; third year, 0.88 c. c. more. (2) Sudden pressure and temperature changes never produced a noticeable evaporation of adsorbed carbon dioxide. (3) Sudden change of pressure within one atmosphere showed no effect upon the steady course of adsorption. (4) Within a temperature interval of 0.8° to 23° C., rise in temperature favored adsorption and conversely.

Bunsen d then showed that the difference between his results and those of Kayser lay in the method used to dry the glass fiber. At ordinary temperature glass may retain even in very dry air (over P_2O_5) a layer of water as thick at 10.55×10^{-6} mm., and at 107° C. up to 7.03×10^{-6} mm.

Thus it is easy to understand why pressure changes within one atmosphere show little or no effect upon the rate of formation of these thin films where the pressure amounts to hundreds of atmospheres. Likewise the solution of gases in these thin films under high

a Forsch. Geb. Agr.-Phys., 15, 201 (1892).

^b Ann. Phys. Chem., **14**, 450 (1881).

c Ann. Phys. Chem., 20, 545 (1883); 22, 145 (1884).

d Ann. Phys. Chem., 24, 321 (1885).

pressure appears reasonable, as well as the long period of time necessary for the establishment of equilibrium.

Mülfarth a has investigated the adsorption of gases by glass powders, with the following results: (1) Perfectly dry glass powder adsorbs a considerable mass of carbon dioxide. This is contrary to the experimental results of Krause.^b (2) Glass powder dried at 420°C. and rendered free from gas shows an adsorption of carbon dioxide as great as glass dried at 500°. (3) The adsorption of the CO₂ by completely dried glass powder is normal; that is to say, it increases with increasing pressure and decreases with increasing temperature. (4) The adsorption of carbon dioxide by dried glass powder is completed in a short time—from one to two hours. (5) The presence of moisture renders the adsorption of CO₂ slower; nevertheless, in a few days it proceeds to completion, and the mass adsorbed is not greatly different from that taken up by dried glass powder at the same pressure and temperature. Consequently, the main influence of dampness appears to consist in rendering the process of adsorption slower. (6) The quantity of carbon dioxide adsorbed is not nearly so great as Bunsen found in his research using glass fiber. (7) The adsorption of sulphur dioxide by dried glass powder proceeds exactly like that of carbon dioxide, is completed in two hours, increases with increasing pressure, and decreases with increasing temperature. (8) At zero degress the following gases are adsorbed by glass powder and in the following order: Ammonia, sulphur dioxide, carbon dioxide, nitrous oxide (N₂O), acetylene, in descending series. The gases, sulphur dioxide and ammonia, which are most easily condensed to liquid, are the most strongly adsorbed. Nitrous oxide and carbon dioxide. which stand very near to each other in respect to the ease of their condensation at low pressures, are almost equally well adsorbed, but carbon dioxide a little more strongly. (9) Henry's law holds fairly well also for the adsorption of gas on glass powder.

Absorption of ammonia.

Ammon^c found that ammonia is absorbed by soil constituents as follows: Humus at 20° C., 11.5 per cent of its dry weight; ferric hydroxide, 4.7; quartz powder, 0.295; calcium carbonate, 0.23; kaolin, 0.42. When pure ammonia gas is absorbed, small quantities of nitric acid are formed, relatively more in ferric hydroxide than in the other soil constituents. The absorption of ammonia in general decreases with increase in temperature, but near zero, Centigrade, the maximum quantity of gas is taken up, less being absorbed at lower as well as at higher temperatures. In view of the more recent work by Dewar^d and others on the absorption of gases at low temperatures the actual existence of such a maximum as Ammon found is open to question.

a Ann. Phys. (4), 3, 328 (1900).

b Ann. Phys. Chem., 36, 923 (1889).

c Forsch. Agr.-Phys., 2, 34 (1879).

d Chem. News, 94, 174 (1906).

Von Dobeneck a has confirmed Ammon's conclusion that the absorption of ammonia is less the higher the temperature when working above zero, Centigrade. Von Dobeneck's quantitative measurements on the absorption of ammonia are in general of the same order of magnitude as those given by Ammon, and in addition von Dobeneck has shown that mixtures of soil constituents absorb ammonia and other gases additively, each material exerting its absorption effect independently of the others. He showed, too, that where a moist powder absorbs ammonia, the quantity of gas retained is very considerably in excess of what the water can dissolve when separate from the powder. Thus, 100 grams water dissolved 43.9 grams of ammonia, but when this same mass of water was held by 854 grams of

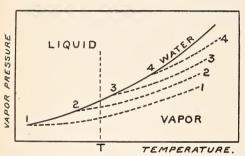


FIG. 9.—Curves showing vapor pressure of water, and of moist soils at various temperatures for case I, assuming that absorption increases with rise in temperature.

kaolin, 56.5 grams of ammonia were absorbed, an increase of 28.6 per cent; with 472 grams kaolin and 100 grams water, 55.7 grams ammonia were absorbed. Similarly the following powdered solids, each wet with 100 grams water absorbed ammonia: 445 grams calcium carbonate, 54.6 grams; 435 grams quartz, 53.1 grams; 329

grams kaolin, 54.0 grams; 200 grams ferric hydroxide, 47.2 grams; 202 grams humus, 78.5 grams; 186 grams kaolin, 51.9 grams.

Schlösing^b found that soils, whether acid or alkaline, dry or wet, absorbed ammonia from the atmosphere in appreciable amount. Calcium carbonate in the soil increases the absorption capacity of the soil for ammonia. Absorption is in a high degree dependent upon a continual renewal of air at the surface of the soil, consequently, it makes a difference whether the surface be bare or covered with vegetation, since the plants tend to prevent circulation of the air in a layer near the surface.

Pfeiffer showed that equal changes in pressure produce about equal changes in the quantity of gas absorbed by different sorts of carbon. He found that the absorption of ammonia by charcoal decreased about one-half on heating from 0° to 70° C.

Absorption of hydrogen.

The absorption of hydrogen is of minor importance from the standpoint of soil chemistry. Joulin^d showed that ignited charcoal absorbs hydrogen so rapidly as to render difficult a measurement of the veloc-

^a Forsch. Agr.-Phys., **15**, 201 (1892). ^b Compt. rend., **110**, 429, 99 (1890).

c Über die Verdichtung von Gasen durch feste Körper; Inaug. Diss. Erlangen (1882).

d Compt. rend., 90, 741 (1880).

ity, and recently Travers^a has studied the absorption of hydrogen by cocoanut charcoal at different temperatures. The numerous investigations on the absorption of hydrogen by metals need only be mentioned in this connection.^b

EFFECT OF TEMPERATURE UPON ABSORPTION.

THEORETICAL CONSIDERATIONS.

Assuming for the particular substance, water, that the quantity of moisture absorbed by a soil from a saturated atmosphere varies with the temperature, there are two possible cases:

(1) The amount of water absorbed increases with the rise in temperature. For this case the vapor-pressure-temperature curves for the soils will cut the vapor-pressure-temperature curve for water, as shown in figure 9; this has apparently been realized experimentally by Hilgard.°

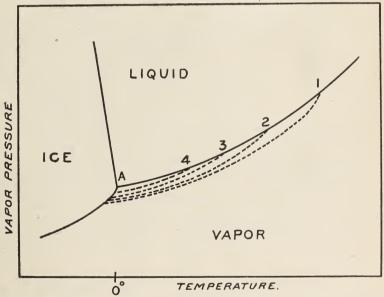


Fig. 10.—Curves showing vapor pressure of water, and of moist soils at various temperatures for case II, assuming that absorption decreases with rise in temperature.

(2) The amount of water absorbed from a saturated atmosphere decreases with rise in temperature. This case is illustrated by figure 10. Here the lower limit of the vapor-pressure curves for soils is the vapor-pressure-temperature curve for ice, and the maximum quantity of water absorbed at any temperature whatever is the mass of water which can remain adsorbed by the soil, in equilibrium with

a Proc. Roy. Soc. London, 78, Ser. A, 9-22 (1906).

b See Fischer, Ann. Phys. (4), 20, 503 (1906).

c "Soils," pp. 196, 198 (1906).

the complete system—ice, "liquid water," water vapor, which exists at the triple point A. The dotted curves in figure 10 show the vapor-pressure-temperature curves for soils. The quantity of moisture in the soil remains constant along the dotted curve, which is limited in extent; above, it meets the vapor-pressure curve of liquid water; below, it cuts the vapor-pressure curve for ice. Here the absorbed water would begin to freeze at a lower temperature than free water; and when we remember the enormous stress under which water exists when in adsorbed condition, this conclusion is not surprising.

EXPERIMENTAL DATA AND DISCUSSION.

Four series of preliminary experiments were carried out. In the first three series 10-gram samples of dry quartz flour, Podunk fine sandy loam, and Sea Island cotton soil were brought to equilibrium with water vapor in desiccators at various temperatures in the thermostat. The

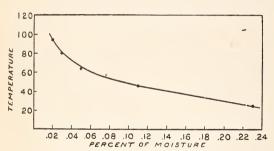


Fig. 11.—Curve showing decrease in absorption of water vapor by quartz flour with rise in temperature.

general trend of these results serves very well to show that the mass of water vapor absorbed decreases with the temperature. And by comparison of this series for Sea Island cotton with a later series for the same soil under rigid conditions, using stop-

pered weighing bottles to avoid loss of moisture on the balance, the exact experimental error is seen at each point.

The results for quartz flour given in Table XIII and plotted in figure 11 show a decrease of 91 per cent in the water absorbed for an increase of 74° C.

Table XIII.—Decrease of absorption with temperature rise for quartz floura in open dish over water.

Temper- held by soil. **C. Per cent. 23 0.23 43 .11 62 .05 80 .03		
23 0. 23 43 . 11 62 . 05		held by
43 . 11 62 . 05	°C.	
	43	. 11

a The same sample was used throughout.

Table XIV.—Decrease of absorption with temperature rise for Podunk soil in open dish over water.

Temper-ature.	Water held by soil.
°C _* 25 43 62 80	Per cent. 0, 81 . 35 . 16 . 11

Table XV.—Decrease of absorption with temperature rise for Sea Island cotton soil in open dish over water.

Temper- ature.	Water held by soil.
°C.	Per cent,
25	8, 4
62	4, 84
80	3, 84

Table XVI.—Decrease of absorption with temperature rise for Sea Island cotton soil in weighing bottles over water.

Temper- ature.	Water held by soil.
°C. 25 100	Per cent. 9. 7 5. 5 5. 4

Podunk fine sandy loam confirms the general trend shown by quartz, as seen in Table XIV and figure 12. The soil absorbs over 50 per cent less water vapor at 43° than at 25°, and a rise in tempera-

ture of only 55°, from 25° to 80°, reduces the moisture content at equilibrium by 86 per cent. Sea Island soil in open dishes over water shows in Table XV a decrease in absorption of 42 per cent for a rise of 32°, and of 54.2 per cent for 55°.

A fourth series for Sea Island cotton soil is given in Table XVI. The quan-

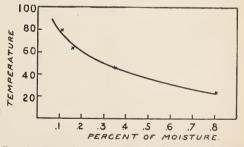


Fig. 12.—Curve showing decrease in absorption of water vapor by Podunk soil with rise in temperature.

tity of water absorbed at 25° over water in a desiccator was determined, using a 20-gram sample in a weighing bottle which could be closed during the weighing to avoid evaporation. The data for

this point are taken from the lower half of Table IV and were obtained under accurately controlled temperature conditions; the equilibrium conditions were established after a run of ninety-seven days.

The absorption at 100° C. was found by inclosing the weighing bottle with its 20-gram soil sample in a sealed tube over water. This

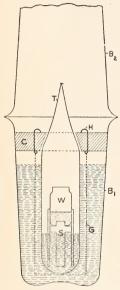


Fig. 13.—Diagram of apparatus used to determine absorption of water vapor by soil at the boiling point of water.

tube was immersed in boiling water, as shown in figure 13, where T is the sealed tube; W, the weighing bottle; S, a copper support to hold the bottle out of the water; G, a safety guard of gauze surrounding the tube T and also serving as a support; C, a cork support for T and G; H, hooks holding the gauze G to the cork C; B₁, a beaker containing boiling water nearly to the level of the cork C; B₂, a tall beaker inverted over B₁ and serving as a condenser.

With this arrangement water need be added to B₁ only every two days. On account of the high temperature, absorption proceeded rapidly to completion; equilibrium was established within a week, as shown by the values given in Table XVI. After one week 5.5 per cent of moisture had been absorbed, and another week's run gave practically the same value, 5.4 per cent; so the system had come to equilibrium. The difficulty met with in the other experiments, Tables XIII, XIV, and XV, did not enter here, since a closed weighing bottle was used.

The data for the two points in Table XVI are shown in figure 14 as curve 1, and for comparison the data from Table XV are given on the same plot and to the same scale, with temperature as ordinate and

percentage moisture in the soil as abscissa. It is evident that the determinations made in open dishes, curve 2, show less moisture than those made in weighing bottles, curve 1. At 80° C. this loss of absorbed moisture from an open evaporating dish during weighing amounts to nearly 40 per cent, at 25° C. this

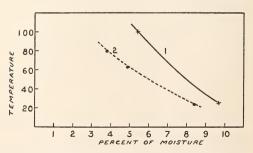


Fig. 14.—Curve showing decrease of absorption of water vapor by Sea Island cotton soil with rise of temperature.

loss is 13 per cent, and for 100° C. extrapolation of curve 2 indicates a loss of some 48 per cent of the total. The curves in figs. 11,

12, and 14 show the same general trend, and together with the most accurately determined points in Table XVI and curve 1, figure 14, show a decrease of absorption as temperature rises in a manner not open to question. All of these curves bend upward steeply at higher temperatures, since the absorbed moisture is held more firmly the thinner the layer in which it is spread upon the soil grains.

Thus it is proved experimentally that absorption of water vapor by soils decreases very greatly with rise in temperature. A departure from equilibrium conditions, which indeed seldom obtain in the field, shows even greater decrease in the quantity of absorbed water as the temperature increases.

ABSORPTION CAPACITY.

It is of interest to see how the absorption data are related to the surface presented by the grains of the different soils used. For this purpose a general survey of the quantity of vapors absorbed by some of the soils studied in the foregoing sections is given in Table XVII.

Unfortunately the area of a soil as calculated from its mechanical analysis (Table XVIII) can give only an approximate result, probably much below the true value. Thus in Table XVII it is seen that Galveston clay absorbs three times the mass of water vapor that Marshall silt loam takes up, while the calculated area of the clay is not three times as great but less than a third greater than the silt loam. The results obtained with toluene were in general similar to those obtained with water. The ether vapor behaves differently, the clay taking in a smaller quantity than would be predicted from the water and toluene results.

Table XIX contains the calculated thickness of the layer of liquid absorbed upon the grains of each soil. The following assumptions were made in deriving these values: (1) That the film of absorbed vapor is uniform in thickness over all the soil grains; (2) density of water, 1; density of toluene, 0.89; density of ether, 0.73; as these densities are probably lower than the density of the surface film the value for the thickness of film is probably too high; (3) density of individual soil grains, 2.5; (4) that the soil grains are spheres; this assumption probably gives a value of the film thickness much too high; (5) that the fractions in the mechanical analyses are clean separations. In the last two fractions the diameters of the grains vary within relatively wide limits. The area of the soil grains is probably several times greater than the value given in Table XVII. For example, the quantity of water absorbed by Galveston clay is much greater than would be expected from its area when the absorption capacity of the other soils and their areas are considered. The clay and silt in the Galveston clay greatly increase its surface beyond

that calculable from a mechanical analysis. It was on this account that the soil separate with grains varying only between 0.1 and 0.05 mm. in diameter was used in this series, so that a more accurately determined surface might be used for the determination of its absorption capacity.

Table XVII.—Area of soil grains as related to absorption capacity for vapors.

			absorbed. Ether		absorbed.	Toluene absorbed.	
Soil.	Area per gram.	Eight days.	Maximum.	Eight days.	Maximum.	Eight days.	Maximum.
Galveston clay. Marshall silt loam. Hagerstown loam Quartz flour. Soil separate (0.1–0.05) Norfolk sand	1,260	Per ct. 8.00 2.84 2.90 .35 .67 .29	Per cent. 12.00 4.00 4.50 .80 1.00 .45	Per ct. 4.80 2.86 3.30 .77 .45	Per cent. 6.00 4.00 4.50	Per ct. 4.79 1.62 1.85 .29 .41 .17	Per cent. 1.7

Table XVIII.—Mechanical analyses.

			Average	diameter	of grain.		
Soil.	2-1 mm.	1-0.5 mm.	0.5–0.25 mm.	0.25-0.1 mm.	0.1-0.05 mm.	0.05–0.005 mm.	0.005-0 mm.
Galveston clay Hagerstown loam Marshall silt loam Quartz flour Norfolk sand	0.7	Per cent. 1.5 3.0 2.8 .0 6.3	Per cent. 0. 40 2. 10 1. 70 . 05 22. 20	Per cent. 7.0 6.5 4.3 .2 63.7	Per cent. 28. 9 13. 9 12. 9 8. 0 4. 1	Per cent. 30. 1 54. 3 56. 9 86. 2 1. 0	Per cent. 31, 00 19, 10 19, 50 5, 42 1, 80

Table XIX.—Comparison of absorption capacity of soils for vapors.

Soil.	Vapor.	Total quantity absorbed.	Quantity per sq. cm. × 105.	Thickness of layer.	Energy = latent heat × grams absorbed.
Soil separate (0.1-0.05), 8 days absorption. Galveston clay, maximum absorption. Marshall silt loam. Hagerstown loam. Norfolk sand. Quartz flour.	Water Toluene Ether Toluene Ether Toluene Ether Toluene Ether Toluene Ether Toluene Ether Toluene	Grams, 0.6417 .4049 .770 12.00 6.00 4.00 1.70 4.00 4.50 4.00 .450 2.5 62 .80 .40	Grams. 2.00 1.26 2.40 3.66 1.83 1.72 .73 1.72 1.98 .82 1.68 1.50 .83 2.06 .64 .32	Cm. × 10 ³ . 2.00 1.42 3.25 3.66 2.06 2.51 1.72 .82 2.35 1.98 .92 2.31 1.50 2.83 64 2.83	378. 2 33. 8 65. 8 7,080. 0 501. 0 2,360. 0 240. 0 345. 0 2,655. 0 155. 0 345. 0 265. 5 20. 9 53. 5 471. 0 334. 0

Table XIX.—Comparison of absorption capacity of soils for vapors—Continued.

Soil.	Vapor.	Vapor pressure.	Temper- ature.	Surface tension.	Viscos- ity.	Density.
Soil separate (0.1-0.05). 8 days absorption. Galveston clay, maximum absorption. Marshall silt loam	Water. Toluene. Ether. Toluene. Ether. Toluene. Ether. Toluene.	Mm. 28. 1 33. 5 575.0 28. 1 33. 5 575.0 28. 1 33. 5 575. 0 28. 1 33. 5 575. 0 28. 1 33. 5 575. 0 28. 1 33. 5 575. 0 28. 1 33. 5			C. G. S. 0.01 .0056 .0024	

This soil separate shows a film 2.0×10^{-5} cm. thick, as against a thickness of 3.66×10^{-5} cm. for Galveston clay and 1.5×10^{-5} for Norfolk sand, while Hagerstown loam and Marshall silt loam give values nearer that of the soil separate. Parks ^a gives a value for the thickness of a water film absorbed on glass wool, 1.34×10^{-5} cm., which agrees closely with these results.

In general, toluene gives a thinner film than water, while the ether layer is thicker than that of water for all soils save Galveston clay.

If we assume the average diameter of a clay particle as 0.0002 cm., and consider it to be a sphere, its volume is 4.19×10^{-12} c. c. If the water film be uniform in thickness over the surface of all the grains, 2.00×10^{-5} cm., as given for the soil separate, then the total volume of this clay particle with its absorbed water will be 7.25×10^{-12} c. c., and the volume of water alone 3.06×10^{-12} c. c., or 73 per cent of the volume of the clay particle holding it, and the radius of the particle is only ten times greater than the thickness of the water layer surrounding it. There is very little doubt that this hygroscopic water is in part held in the fine capillary spaces between the soil grains, but we have no sharp experimental method of ascertaining what fraction of the water is thus retained.

A comparison of the quantities of water, toluene, and ether absorbed by the various soils, with their surface tensions, viscosities, vapor pressures, and latent heats of evaporation does not give a clue to the different absorption capacities found. It seems that each vapor has its own specific action which finds a counterpart in the selective absorption exercised by the soil. For any one vapor the absorption

a Loc. cit.

b Katao, Über die Wasserbewegung in Boden, Bul. Col. Agr., Imp. Univ., Tokyo, Vol. 3, No. 1, 1897; Soyaka, Forsch. Agr. Phys. 8, 1 (1885); Whitney, Agricultural Science, Vol. 3, p. 199, 1889; Briggs, Bul. No. 10, U. S. Dept. of Agriculture, Division of Soils (1897).

capacity of a soil is roughly proportional to the soil grain surface as calculated from the mechanical analysis.

Finally, we see from the above considerations that for any one vapor the amount of absorption is proportional to the calculated soil area exposed, and that the thickness of film on any given soil surface varies with the nature of the vapor, but the data at present available are not sufficient to show that the thickness of the film is dependent upon the nature of the soil type.

DISTRIBUTION.

Solids in general do not completely absorb gases or vapors, but rather the gas is divided between the atmosphere and the solid. The greater the quantity of gas or vapor in the atmosphere, the more of it is held fixed by the solid, until the solid becomes saturated and can retain no more of the gas. A number of attempts have been made to express this relation_between the quantity absorbed by the solid and the concentration of gas in the atmosphere, as a fairly simple mathematical equation. The chemical composition of the solid and that of the gas of course determine in great measure the degree to which absorption takes place, and this factor is expressed by a constant which is different for each solid and gas studied. The effect of temperature upon absorption is likewise recognized in the formula by a constant whose value changes with the temperature.

De Saussure ^a has suggested the formula V = 19.1 + 0.53 P, where V is the volume of gas adsorbed and P is the pressure in inches of mercury. This relation holds for carbon dioxide.

Ostwald b applies to gaseous adsorption the equation, $\frac{x}{m} = \alpha \operatorname{C} \frac{1}{p}$, which was developed for adsorption from solution, where x is the mass of gas adsorbed; m the mass of adsorbent solid; C the concentration of the vapor phase; α is a constant; and $\frac{1}{p}$ is an exponent. Freundlich holds that adsorption from solution and from vapor by solids follow the same law, and Ostwald's exponent, $\frac{1}{p}$ equals $1 - \frac{1}{n}$, where $\frac{1}{n}$ is the exponent in the equation, $\alpha = \alpha \left(\frac{a}{p}\right) - \frac{1}{n}$, proposed by himself.

a Loc. cit.

^b Lehrbuch der Allgemeine Chemie, II (2 Aufl.) 232.

 $c \lambda = \alpha \left(\frac{a}{v}\right)^{-\frac{1}{n}}$ is simply an empirical relation, and is not derived analytically from the other equation, $\lambda = \frac{v}{m} \ln \left(\frac{a}{a-x}\right)$ given by Freundlich. λ and α are constants; a is total mass of gas in the system, and v is the volume of space available for the gas.

Thus Freundlich found working with liquid solutions, values for $\frac{1}{n}$, which range from 0.86 to 0.485, giving to $\frac{1}{p} \left(= 1 - \frac{1}{n} \right)$ values from 0.14 to 0.515. But the $\frac{1}{p}$ given by Ostwald on the basis of Chappuis, a Joulin, and Kayser's results, for CO₂ adsorbed by various kinds of charcoal, is higher, varying from 0.50 to 0.75. Further, Chappuis's curve for $\log \frac{x}{m}$ against C is very concave for carbon dioxide, whereas if the exponential formula $\frac{x}{m} = \alpha$ C $\frac{1}{p}$ applies, this curve should be a

straight line. So this formula of Ostwald's holds only indifferently well as far as this gas is concerned.

Recently Travers d has determined the distribution of hydrogen and of carbon dioxide between cocoanut charcoal and the vapor at 100° , 60° , 35° , 0° and -78° , and for hydrogen at -190° C. He suggests the formula, $\sqrt[n]{p}$ a constant, where P is the gas pressure and x the concentration of the gas, in the solid phase for each temperature. The value of n increases when the temperature falls. For CO_2 at 0° , n=3; at 100° , n=2; at higher temperatures n would probably equal 1 and then the distribution law would hold exactly—i. e., become linear—but it is possible, too, that n might fall below 1. Hydrogen at -190° behaves exactly like CO_2 at 0° ; that is, n=3. Travers attributes the departure of the distribution law from a linear form at low temperatures to the influence of diffusion into the solid phase. On the contrary, Trouton e has assumed the formation of a liquid phase upon the surface of the solid to explain his curves representing the absorption of water vapor by cotton.

It is seen that no one mathematical expression yet proposed describes the present data for the adsorption of gases by solids. The specific attractions of solid and gas, the diffusion of gas into solid, the condensation of gas to liquid, and the consequent clogging of capillary channels where the forms and arrangement of these minute spaces enter to determine the vapor pressure of the liquid there enmeshed, all these factors complicate the observed relation of mass of gas adsorbed to mass of gas left in the vapor phase.

^a Ann. Phys. Chem., **12**, 161 (1881).

b Ann. Chim. Phys. (5), 22, 397 (1881).

c Ann. Phys. Chem., 12, 526 (1881).

d Proc. Roy. Soc. London, 78, Ser. A, 9 (1906).

e Proc. Roy. Soc. London, 77, Ser. A, 292 (1906).

RATE OF ABSORPTION.

DETERMINING FACTORS.

The rate at which a solid absorbs a vapor depends upon several factors. These will be discussed in the following paragraphs.

Chemical composition.

In general, the chemical composition of the solid affects absorption to the extent that acid bodies tend to absorb basic vapors, and conversely. The magnitude of this influence varies from very pronounced chemical reaction, such as the fixation of gaseous ammonia by solid acids to extremely weak acid or basic effects.

Physical condition.

The physical condition of the solid, its fineness of division, determines the surface available for the purely adsorption effect, which, with other conditions the same, is directly proportioned to the surface of the solid in contact with the vapor. As the solid is reduced to finer powder the number of solid angles between the granules is increased, as well as the surface of solid exposed, and the condensed vapor retained in these solid angles is added to that held by simple absorption.

Viscosity of the vapor.

In the case of vapor entering a soil at rest there is a damping term due to the viscosity of the vapor. After taking account of the probable diameter of the capillary spaces through which the vapor is to pass, the resistance which the vapor offers to being forced into the soil is the viscosity of the vapor multiplied by its rate of flow, a and this rate of flow is the rate at which absorption is taking place. The diameters of the capillary spaces, too, become less as the surface of each grain takes on moisture, so the resistance to the passage of vapor increases as the absorption proceeds. Consequently we should expect rate curves for soils to show a decrease in rate of absorption with time greater than that for absorption of vapor upon a plane surface, but this factor has been found to be of only minor import.

Absorption capacity.

The absorption capacity of the solid affects the rate of absorption to a marked degree. Where the absorption capacity is high, the speed of absorption is very great.

^a See E. Wollny, Forsch. Agr.-Phys. **16**, 193 (1893); Buckingham, Bul. No. 25, Bureau of Soils, U. S. Dept. Agr. (1904).

Partial pressure, or humidity.

The rate of absorption of water by soils varies for atmospheres of different humidity in a manner similar to the change in rate of evaporation under different degrees of humidity, as can be seen from the curves in figure 15 for Sea Island cotton soil plotted from the data given in the lower half of Table IV. Ordinates are in percentage of moisture in the soil, abscissas are in time in days. All the experiments begin at 4.4 per cent of moisture, the quantity retained by Sea Island cotton soil in air-dry condition.

Van Bemmelen,^a Hellriegel,^b Puchner,^c and von Dobeneck ^d have determined the speed with which a soil absorbs water vapor.

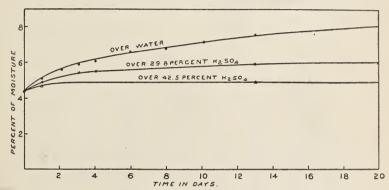


Fig. 15.—Curves showing rate of absorption of water vapor by Sea Island cotton soil under different degrees of humidity.

They, too, give very regular rate curves, but these, as well as Parks e rate of absorption of water vapor by glass wool, are likewise not described by a simple mathematical formula. Hantzsch has shown that the rate of absorption of ammonia gas by solid organic acids in finely powdered condition depends upon the partial pressure of the ammonia gas in the atmosphere above the solid acid. Using absolute ammonia, the reaction is fairly well described by the

first order reaction velocity equation, $K^{I.} = \frac{1}{t} \log \left(\frac{a}{a-x}\right)$, and on dilution of the ammonia with air, this equation still holds if the total volume of gas employed is so great that the partial pressure of the ammonia is practically constant throughout the absorption process.

If, however, the quantity of ammonia present in the gas is considerably reduced by the absorption, then the rate of absorption is

a Arch. Néer. (2), 10, 267 (1906).

b Forsch. Agr.-Phys. 6, 389 (1883).

c Land. Vers.-Stat., 46, 229 (1895).

d Forsch. Agr.-Phys., 15, 163 (1892).

c Phil. Mag. (6), 5, 518 (1903).

f Zeit. phys. Chem., 48, 289 (1904).

no longer expressed by this first order reaction velocity equation, but is more nearly given by the second order equation, $K^{II} = \frac{1}{t} \frac{x}{(a-x)a}$. The same is true for the absorption of gaseous hydrogen chloride by solid organic bases. A similar effect is produced in the rate of absorption of water vapor by a soil as the atmospheric humidity varies.

The rates of absorption of water vapor by humus from atmospheres saturated at different temperatures, as determined by von Dobeneck (Table XX), show, too, that the velocity of absorption is greater the higher the relative humidity.

The rate curves obtained from all of the foregoing tables are regular, but are not described by a simple velocity equation.

Table XX.—Rate of absorption of water vapor by humus, according to von Dobeneck.

Dominal		Q	iantity of	water abs	orped at—		
Period.	a 0° C.	a 10° C.	<i>a</i> 20° C.	<i>a</i> 30° C.	<i>b</i> 10° C.	<i>b</i> 20° C.	<i>b</i> 30° C.
Days.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent
1	0.12	1.40	1.96	3.59	1.35	1.61	2.14
2	. 50	2.47	3, 22	6.27	2.22	2.48	2.29
3	. 88	3.61	4.84	8.13	3.24	2.99	2.32
4	1.25	4.57	5.77	10.03	4.37	3, 47	2.36
5	1.79	5, 44	7.11	11.17	5.28	3, 63	2.39
6	2.28	6.19	8.33	12.39	6.17	3.77	2,43
7	2.79	7.01	9.36	13.61	6.76	3.92	2.42
8	3.30	8, 11	10.18	14.20	7.28	4.01	2.45
9	3.76	8.76	10.88	14.65	7.61	4.08	2.49
10	4.23	9.34	11.39	15.34	7.91	4.13	2.48
12	5.06	9.65	12.51	15.98	8.32	4.15	2.10
14	5.95	10.37	13.32	10.00	8. 49	1.10	
16	6.89	11.13	14.03		8.60		
18	7.60	12.02	14.64		8.63		
20	8.32	12.83	15.02		0.00		
22	9.09	13.62	15.28			,	
24	9.90	14.20	15.56				
26	10, 61	14.70	15.86				
28	11.22	15.03	15.89				
30	11.83	15.38	10.00				
32	12, 43	15.68					
34	12.96	15.95					
36	13.48	10.00					
38	13.99						
- 40	14.46						
42	14.89						
44	15.25						
46	15.59						
48	15.79						
50	15.90	(

^a Atmosphere saturated with moisture at temperature given. ^b Atmosphere saturated with moisture at 0°.

Previously absorbed vapor.

As will be seen from the data on the rate of absorption of vapors by soils in Tables II, III, IV, V, VI, VIII, IX, X, and XI, the rate of absorption decreases as more and more vapor is held by the soil. This effect is only what would be expected when we remember that the last portions of vapor absorbed and condensed to liquid form exist to a considerable extent in the capillary spaces of the soil as well as in the form of films upon the surface of the soil grains.

Temperature.

(a) It has been shown by the investigations cited above and by the new experiments given in the section on the effect of temperature upon absorption, that in saturated atmospheres, at least, an increase in temperature decreases the mass of vapor absorbed by a solid. (b) Increase in temperature increases the mass of vapor which a given volume of air can hold at any one pressure. Theoretically, then, the first temperature effect (a) should reduce the time required to saturate the absorbing solid with vapor; and the second effect (b) should likewise hasten the absorption by providing a higher absolute quantity of vapor in the atmosphere for the solid to draw upon. conclusion is borne out experimentally by the results obtained with Sea Island cotton soil; at 100° C. only one week was required for this soil to absorb all the vapor it could take up, whereas at 25° C, this same soil stood ninety-seven days over water before it ceased to absorb moisture. Von Dobeneck a confirms this effect of temperature upon rate of absorption as shown in Tables VII and XX.

Joulin^b found that the time required to saturate charcoal with carbon dioxide decreased with increasing temperature at a constant

pressure.

RATE OF EVAPORATION.

In a former bulletin the mechanism of evaporation has been discussed in considerable detail.^c In addition to the data on the evaporation of moisture from soils under various degrees of humidity, which have been given in Tables II, III, and IV, above, we repeat here

in Tables XXI, XXII, XXIII, XXIII, and XXIV the data in that bulletin on the rate of evaporation from wet soils over concentrated sulphuric acid at 25° C. The point brought out by the evaporation data in all of these tables is that the rate of evaporation from any wet soil is fairly constant until the quantity of moisture still remaining in the soil is approximately that known as the "opti-

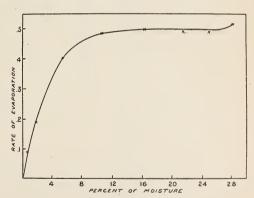


Fig. 16.—Curve showing rate of evaporation of water from Podunk soil.

mum water content" of the soil. At this point a gradual change in the rate of evaporation takes place, as shown in figures 16, 17, 18, and 19, which represent graphically the rate of evaporation indicated in Tables XXI, XXII, XXIII, and XXIV. Referring back to figures 1, 2,

a Loc. cit.

b Comp. rend., 90, 741 (1880).

c Cameron and Gallagher, Bul. 50, Bureau of Soils, U. S. Dept. Agr., 1907.

and 3 we see this same bend in the rate of evaporation curves, which becomes less and less evident as the humidity of the atmosphere of the soil approaches the saturation point, going from the par-

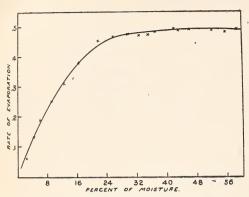


Fig. 17.—Curve showing rate of evaporation of water from Miami soil.

tial pressure of water vapor of 94 per cent sulphuric acid up to that of the vapor pressure of water alone. As was stated in Bulletin 50, the moisture content of each of these soils at which this bend in the rate of evaporation takes place is in reality very close to the content of water in the soil which gives it the best physical condition for plant growth.

The reason for this agree-

ment between the point at which the rate of evaporation changes and the point known as the "optimum water content" has been also pointed out in Bulletin 50. The larger open spaces between the soil grains naturally lose their water first, and the later portions of water evaporate more and more from the finer capillary spaces in

the soil. When the water content of the soil is reduced to such a degree that the loosely held water in these more open spaces must draw upon the water held as a capillary film upon the soil grains, then very naturally evaporation proceeds more slowly,

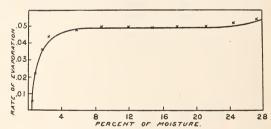


Fig. 18.—Curve showing rate of evaporation of water from Leonardtown soil.

since the films are held by the soil grains quite tenaciously. At this same moisture content, too, where the pull of the capillary films of water upon the soil grains is brought into evidence, we would naturally expect that the very fine soil particles might be rearranged into larger aggregates and thus furnish a more open structure better suited for access of atmospheric gases and for the penetration of roots.

In this connection it is interesting to note that Heinrich^a has shown that the quantity of water in a soil required for plant growth is always greater than the quantity of water the soil can take up

 ^a Zweiter Ber. landw. Vers.-Stat. Rostock, p. 19 (1894): E. S. R., 7, 481 (1895-96).
 See also Spalding, Bot. Gaz. 38, 122 (1904).

from a saturated atmosphere. A heavy soil containing a high percentage of moisture may hold the water so absorbed that while the plant can get some water, still it is by no means fully supplied.

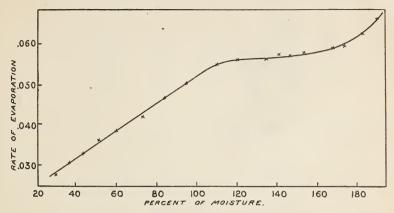


Fig. 19.—Curve showing rate of evaporation of water from muck soil.

Table XXI.—Rate of evaporation from Podunk fine sandy loam over 95 per cent sulphuric acid at 25° C., according to Cameron and Gallagher.

Mean moisture content.	Period.	Loss of moisture.	Loss per hour.
Per cent. 27. 4 24. 2 21. 3 17. 8 14. 8 12. 0 8. 7 5. 8 2. 4 1. 7 0. 9 0. 3	Hours. 19.5 4.5 18.7 9.3 15.3 9.9 14.5 9.9 4.0 2.0 11.0 2.0	Grams. 1.0450 2362 9210 4595 7495 4854 7140 4712 1732 0719 2445 .0097	Grams. 0.0563 0.0525 0.493 0.0494 0.0490 0.0490 0.0492 0.0476 0.0433 0.0359 0.0222 0.0049

Table XXII.—Rate of evaporation from Miami black loam over 95 per cent sulphuric acid at 25° C., according to Cameron and Gallagher.

Mean moisture content.	Period.	Loss of moisture.	Loss per hour.
Per cent. 58. 5 55. 4 49. 4 46. 4 43. 4 41. 0 37. 5 35. 4 29. 7 26. 9 17. 1 12. 9 9. 5 6. 7 5. 1 3. 7 2. 7	Hours. 16. 70 9. 30 15. 17 9. 90 14. 50 9. 90 11. 00 6. 50 7. 00 17. 50 24. 00 24. 00 24. 50 22. 25 24. 50 22. 75 23. 75 24. 25	Grams. 0. 8198 4474 4474 44802 4802 7155 4808 5427 5441 3099 8295 3321 7964 1. 0879 9.109 8108 5716 4094 3056 2136	Grams. 0.0491 .0481 .0489 .0485 .0493 .0486 .0492 .0483 .0477 .0474 .0474 .0468 .0453 .0379 .0309 .0257 .0192 .0134 .0990 .0061

Table XXIII.—Rate of evaporation from Leonardtown loam over 95 per cent sulphuric acid at 25° C., according to Cameron and Gallagher.

Mean moisture content.	Period.	Loss of moisture.	Loss per hour.
Per cent. 28.2 24.9 21.6 16.4 10.7 5.5 2.0 .7	Hours. 19. 00 7. 25 19. 25 22. 00 24. 50 22. 75 24. 25 24. 16	Grams. 0.9770 .3555 .9538 1.0962 1.1963 .9193 .4560 .0904	Grams, 0. 0517 0490 0495 0498 0488 0404 0188 0037

Table XXIV.—Rate of evaporation from muck over 95 per cent sulphuric acid, at 25° C., according to Cameron and Gallagher.

Mean moisture content.	Period	Loss of moisture.	Loss per hour.
Per cent. 190 183 183 174 168 154 147 141 135 121 110 95 84 74 60 52 44 37 30	Hours. 9, 50 15, 20 9, 85 14, 50 10, 00 13, 00 6, 50 17, 50 17, 50 24, 00 24, 00 26, 30 22, 10 24, 30 23, 00 24, 00 24, 00 24, 00 24, 00 24, 00 24, 50	Grams, 0. 6362 9590 5905 8639 5813 7474 3744 9893 9591 1. 3233 1. 2332 9329 9388 8352 7958 7372 6851	Grams. 0.0669 0.6632 0.600 0.596 0.581 0.576 0.576 0.566 0.564 0.551 0.0505 0.469 0.423 0.387 0.363 0.331 0.307

ENERGY CHANGES.

Poggendorff attributes the first experimental work on capillarity to Leonardo da Vinci, 1452–1519. A number of investigators a worked in the field before it was discovered that capillary phenomena are accompanied by heat effects. De Saussure b during 1812 to 1814 found that heat was evolved during the process of absorption.

Pouillet c showed the rise in temperature of various powders and porous substances when moistened with a liquid. Unfortunately, he, as well as several investigators following him, neglected to communicate the weight of powder and of liquid used and their specific heats; so we are unable to calculate the quantity of heat set free. He gives merely the rise in temperature produced by adding liquid to the material, using water, oil, alcohol, and ethyl acetate with

a Ann. Phys. (Gilbert's), 47, 113 (1814).

^b For a more extended survey of the literature see Trans. Am. Electrochem. Soc., 11, 387 (1907).

c Ann. Chim. Phys., 20, 141 (1822); Ann. Phys., 73, 356 (1823).

finely divided metals, metallic oxides, powdered glass, clay, and other substances, including a number of organic solids. Water added to inorganic solids gave a rise of 0.2° to 0.6° C., while with dried organic material the temperature rise sometimes reached 10° C.

Ammon a cites the observations of Von Babo on the rise in temperature experienced by dry soils when subjected to an atmosphere saturated with water vapor. These experiments are qualitative only, but they show the existence of the heat effect due to moistening a powder; that it is positive, and that the temperature rise is greater with soils containing humus than without.

Stellwagg c found a marked increase in the temperature on moistening various soils and soil constituents with water and on subjecting them to humid atmospheres. But he has given no data enabling us to calculate the number of calories liberated during this adsorption; consequently his data have only qualitative value. He concludes: (1) That the rise in temperature which the soil experiences upon addition of water, in general is greater the drier the soil, the finer its grains, and the lower the prevailing temperature. (2) That the rise of soil temperature on addition of water to a perfectly dry soil is very considerable (8.33° C. for a calcareous sand rich in humus, 6.6° C. for ferric hydroxide, 5.57° C. for a loam soil). (3) That when water vapor is adsorbed by soil constituents a temperature rise is observed as follows: Quartz sand, 0.00-0.25 mm. diameter, 0.88°; quartz powder, 1.08°; precipitated calcium carbonate, 1.47°; kaolin, 2.63°; ferric hydroxide, 9.30°; peat, 12.25° C. (4) That the temperature rise due to adsorption of dry carbon dioxide by dry soil constituents is inconsiderable, with the exception of ferric hydroxide, in which case the rise is 6.9° C., while the moist gas is adsorbed with a much greater temperature increase. (5) That dry soil constituents adsorb dry ammonia and experience a considerable temperature rise: Quartz powder, 0.80°; precipitated calcium carbonate, 0.80°; kaolin, 2.05°; ferric hydroxide, 18.05°; peat, 28.3° C. Moist ammonia shows less temperature rise; for ferric hydroxide and for peat it is, respectively, 14.1° and 23.80° C.

This heat evolved when a vapor condenses upon a solid absorbent was very naturally attributed to the latent heat of vaporization which became available on liquefaction. But Favre d found the heat liberated by absorption to be greatly in excess of the latent heat of vaporization, for three different gases; consequently, this assumption had to be abandoned. More recently Deware has shown

a Forsch. Agr.-Phys., 2, 21 (1879).

b Mülder, Chemie der Ackerkrume, Band 3, p. 366.

c Forsch. Agr.-Phys., 5, 211 (1882).

d Lehmann, Molecular-Physik. I, p. 85.

chem. News. 94, 174 (1906); Proc. Roy. Soc., 74, 130 (1904).

that hydrogen, whose latent heat of vaporization at its boiling point is 120 gram calories, gives off six times that quantity of heat when absorbed by charcoal at the boiling point of air. Similarly, oxygen gas when absorbed by charcoal liberates twice the heat due to liquefaction.

The experiments of Parks a indicate that the quantity of water absorbed by a powder from water vapor is very nearly the same as the quantity of water held on the surface of the grains when the powder is immersed in liquid water. He has shown that a silica powder saturated with water vapor gives off no measurable heat when brought into contact with liquid water, whereas the dry silica liberates a definite quantity of heat per square centimeter of surface, and this heat evolution decreases in a perfectly regular manner as the silica powder contains more and more absorbed water vapor.

Masson^b has shown that the heat evolved when cotton absorbs water vapor is for practical purposes directly proportional to the quantity of moisture absorbed and is very nearly the same as the latent heat of vaporization. He finds the absorption by cotton to be much greater than is warranted by its area as compared with similar experiments using glass wool, and suggests as an explanation that the water absorbed penetrates into the cotton fiber as a solid solution. The thermal effect dealt with here is evidently different from that studied by Parks.^c

When a gas is absorbed by a metal many interesting physical changes in the metal may be effected. Its volume, hardness, elasticity, electrical conductivity, and single potential and rate of solution in various solvent liquids are changed. The absorption of a gas, too, may depend upon its condition; that is to say, the energy it possesses. For example, free hydrogen gas is very slightly absorbed by iron and some other metals, but hydrogen freshly liberated from combination either by electrolysis or by action of metal upon acid is very strongly absorbed by iron. Palladium, on the other hand, absorbs free hydrogen with great avidity.

SUMMARY.

In the absorption of water vapor by quartz flour, a soil separate, and typical soils, the rate of approach to equilibrium between soil and water vapor has been followed at various degrees of humidity, and these equilibrium points determined.

The amount of water absorbed increases with the humidity, but not in a simple mathematical relation.

a Phil. Mag. (6), 5, 521 (1903).

b Proc. Roy. Soc. London, 74, 249 (1904-5).

c Loc. cit.

Toluene and other vapors were compared with water vapor, using the same soils, and show in general an absorption of the same order of magnitude.

The velocity of absorption decreases regularly as absorption proceeds, but it is not described by a simple logarithmic equation.

Relatively small decrease in vapor pressure produces a marked increase in the rate at which the soil dries out. At the moisture content known as "optimum" for plant growth, a rapid decrease in the rate of evaporation takes place, and at this particular moisture content there are likewise changes in other physical characteristics of the soil, such as specific volume, resistance to penetration, etc., which altogether point strongly to a purely physical reason for the existence of a narrow range of water content in a soil at which plants thrive best.

The content of water in a soil at which plants begin to wilt is greater than the quantity of water the soil can take up from a saturated atmosphere. A heavy soil containing a high per cent of moisture may hold the water so absorbed that while the plant can get some water still it is by no means fully supplied.

The absorptive capacity of soil for water vapor is generally higher the finer the texture of the soil and the greater the content of humus. In general, productive soils have a very considerable capacity for water vapor.

Gases are absorbed to a different degree by each solid substance; the different soil components all possess a considerable absorption capacity, and mixtures of these constituents absorb gases additively; that is, each soil material exerts its absorptive effect independently of the rest of the soil about it. Soil constituents moistened with water absorb gases in greater quantity than would the same mass of water alone. Easily condensed gases are in general absorbed more easily.

Heat is evolved during the process of absorption, and this heat is greatly in excess of that given out by the condensation of the vapor to a liquid.

For equilibria between soils and atmosphere saturated with water vapor over a temperature range from 25° C. to 100° C., the amount of water absorbed decreases with increasing temperature. This confirms the results obtained by earlier investigators for the absorption of water vapor as well as for gases in general.

Absorbed gases are held with remarkable tenacity. Glass and minerals retain hygroscopic water up to 500° to 800° C.

a See Cameron and Gallagher. Bul. 50, Bureau of Soils, U. S. Dept. of Agr., 1907.

Bodies which have been heated and then cooled in a vacuum show high absorptive power; consequently, absorption can not be looked upon solely as the solution of a gas in moisture films upon the grains of the solid.

In general, nitrogen is absorbed by soils in greater quantity than oxygen. This is especially interesting, since the absorption of oxygen and nitrogen from air by water gives a higher ratio of oxygen to nitrogen in the solution than the 1:4 relation which exists in air. The similar high absorptive power of aluminum hydroxide, ferric hydroxide, and magnesium carbonate for nitrogen indicates that this preference of soils for nitrogen is a real phenomenon, since these substances have no way of masking their true absorptive power for oxygen by converting it chemically to carbon dioxide, as a soil does, or to other oxides.

The absorption of carbon dioxide by soils is due in great measure to the presence of hydrated oxides, such as ferric oxide, and humus. Kaolin, calcium carbonate, and quartz also absorb carbon dioxide, but in comparatively small amounts.

Soils, whether acid or alkaline, dry or wet, absorb ammonia from the atmosphere in appreciable amount.

No one mathematical expression has been found to hold generally for the distribution of a gas between the vapor phase and absorbing solid. The specific attraction of solid and gas, the diffusion of gas into solid, the condensation of gas to liquids and consequent clogging of capillary channels where the forms and arrangement of these minute spaces enter to determine the vapor pressure of the liquid there enmeshed, all these factors complicate the observed relation of mass of gas adsorbed to mass of gas left in the vapor phase.

